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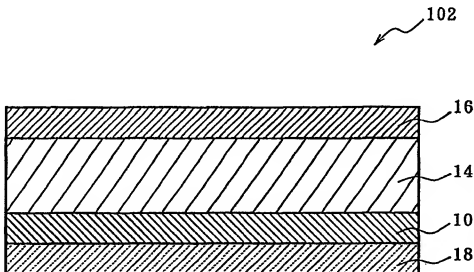
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**Tokyo 100-8321 (JP)****(54) ORGANIC ELECTROLUMINESCENCE DEVICE**

(57) An organic electroluminescence element comprising: an anode layer, a cathode layer, and an organic luminescence layer therebetween, the organic luminescence layer having a carbazole derivative with a glass-transition temperature of 110°C or higher, and a phos-

phorescent dopant. This structure makes it possible to provide an organic electroluminescence element which can make use of the triplet exciton state of the carbazole derivative even at room temperature and which has a practical life and superior heat-resistance.

**FIG. 1**

## Description

## BACKGROUND OF THE INVENTION

## Field of the Invention

[0001] The present invention relates to an organic electroluminescence element (which may be referred to as an organic EL element hereinafter). More specifically, the present invention relates to an organic EL element using a triplet exciton of an organic luminescence material (host material).

## Description of the Related Art

[0002] Hitherto, organic EL elements wherein an organic luminescence layer is arranged between electrodes have been eagerly researched and developed for the following reasons and the like.

- (1) Since these elements are completely solid, they are easy to handle and produce.
- (2) Since they can emit light by themselves, no light emitting members are necessary.
- (3) Since they can be clearly watched, they are suitable for display.
- (4) They permit full color display easily.

[0003] The luminescence mechanism of such organic EL elements generally makes use of a luminescence phenomenon, which is energy conversion phenomenon caused when a fluorescent molecule in a singlet excited state (which may be referred to a S1 state) in an organic luminescence medium is transitioned to a ground state radially.

[0004] A fluorescent molecule in a triplet excited state (which may be referred to a T1 state) in an organic luminescence medium can be supposed. However, radiative transition to a ground state is forbidden; therefore, such a molecule is gradually transitioned from the triplet excited state to some other state by non-radiative transition. As a result, no fluorescence is emitted but thermal energy is radiated.

[0005] Here, singlet and triplet mean multiplicity of energy decided by combination of total spin angular momentum and total orbital angular momentum of a fluorescent molecule. Specifically, a singlet excited state is defined as an energy state in the case that a single electron is transitioned from a ground state, where no unpaired electrons are present, to a higher energy level without changing the spin state of the electron. A triplet excited state is defined as an energy state in the case that a single electron is transitioned to a higher energy level while the spin state of the electron is made reverse.

[0006] Needless to say, luminescence in a triplet excited state defined as above can be observed if the luminescence is caused at a very low temperature, for example, at a liquefaction temperature of liquid nitrogen (-196°C). However, this temperature is not a practical temperature, and the amount of the luminescence is only a little.

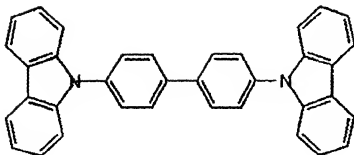
[0007] By the way, the total efficiency of luminescence from any conventional organic EL element is related to recombination efficiency ( $\phi_{\text{rec}}$ ) of injected charged carries (electrons and holes), and the probability ( $\phi_{\text{rad}}$ ) that generated excitons cause radiative transition. Therefore, the total efficiency ( $\phi_{\text{el}}$ ) of luminescence from the organic EL element can be represented by the following equation:

$$\phi_{\text{el}} = \phi_{\text{rec}} \times 0.25\phi_{\text{rad}}$$

[0008] The coefficient (0.25) of  $\phi_{\text{rad}}$  in the equation is decided from the matter that the probability that singlet excitons are generated is regarded as 1/4. Therefore, even if recombination and radiative attenuation of excitons are caused with a probability coefficient of 1, the theoretical upper limit of luminescence efficiency of the organic EL element is 25%.

[0009] As described above, in any conventional organic EL element, triplet excitons cannot be substantially used and only singlet excitons cause radiative transition. Thus, a problem that the upper limit of the luminescence efficiency is low arises.

[0010] Thus, literature 1 "Jpn. J. Appl. Phys., 38 (1999) L1502" discloses that even at room temperature, triplet excitons (triplet excited state) of an organic luminescence material (host material) are used to transfer energy from the triplet excitons to a phosphorescent dopant, so as to generate a fluorescent luminescence phenomenon. More specifically, the literature 1 reports that a fluorescent luminescence phenomenon is caused in an organic EL element comprising an organic luminescence layer composed of 4,4-N,N-dicarbazolylbiphenyl represented by the following formula (6) and an Ir complex, which is a phosphorescent dopant.



(6)

[0011] However, the half-life of the organic EL element described in the literature 1 is below 150 hours, and the usefulness of the organic EL element is insufficient.

[0012] Thus, the inventor made eager investigations. As a result, the following has been found: the glass-transition temperature of 4,4'-N,N-dicarbazolylbiphenyl is as low as less than 110°C; therefore, if the biphenyl is combined with an Ir complex, crystallization is easily caused in the organic luminescence layer comprising the combination to make the life of an organic EL element short.

[0013] Incidentally, in the present situation, a demand that the heat-resistance of organic EL elements for cars should be made higher has been increasing in light of environment inside cars in summer.

[0014] Thus, an object of the present invention is to provide an organic EL element which makes it possible to use triplet excitons of an organic luminescence material (host material) even at room temperature to emit fluorescence (including phosphorescence); has a practical life span; and has a superior heat-resistance.

#### SUMMARY OF THE INVENTION

##### [0015]

[1] According to the present invention, provided is an organic EL element comprising:

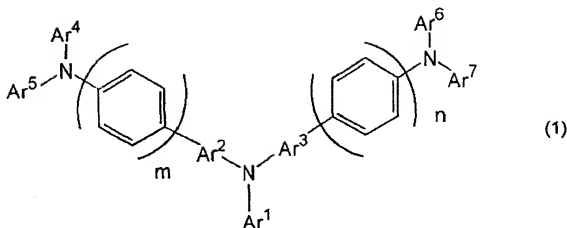
an anode layer,

a cathode layer, and

an organic luminescence layer therebetween, the organic luminescence layer having a carbazole derivative with a glass-transition temperature of 110°C or higher, and a phosphorescent dopant. Thus, the above-mentioned problems can be solved.

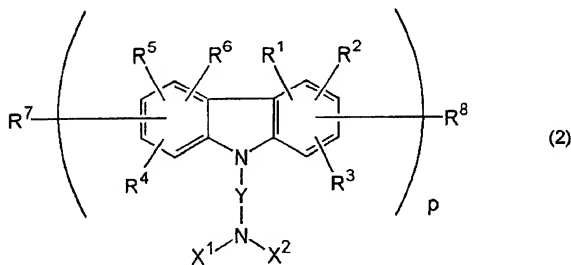
This organic EL element makes it possible to use the triplet exciton state of the organic luminescence material even at room temperature. Moreover, this element has a practical life, for example, a half-time of 300 hours or more, and has superior heat-resistance. Thus, this element can be sufficiently used as an organic EL element for car.

[2] In the organic EL element of the present invention, it is preferred that the carbazole derivative is at least one of compounds represented by the following general formulae (1) to (4):



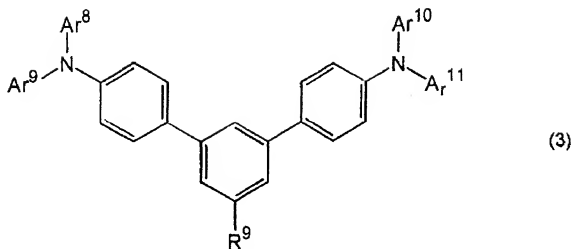
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wherein Ar<sup>1</sup> is a substituted or non-substituted aryl group having 6 to 50 nucleus carbon atoms; Ar<sup>2</sup> to Ar<sup>7</sup> are each independently a substituted or non-substituted aryl or arylene group having 6 to 50 nucleus carbon atoms; Ar<sup>2</sup> and Ar<sup>3</sup>, Ar<sup>4</sup> and Ar<sup>5</sup>, or Ar<sup>6</sup> and Ar<sup>7</sup> may be connected to each other through a single bond or through O, S or substituted or non-substituted alkylene as a connecting group; and each of repetition numbers m and n is an integer of 0 to 3,

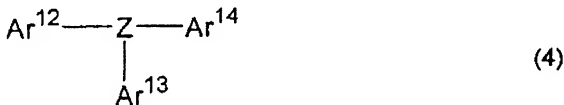


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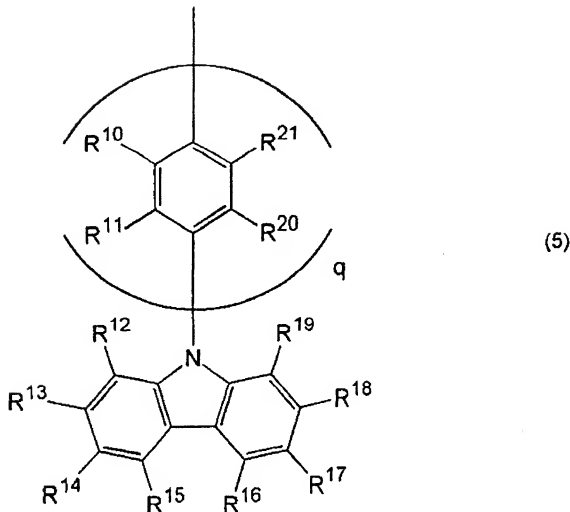
wherein R<sup>1</sup> to R<sup>6</sup> are each independently a hydrogen or halogen atom, an alkyl, aralkyl, aryl, cycloalkyl, fluoroalkyl, amino, nitro, cyano, hydroxy, or alkoxy group; R<sup>7</sup> and R<sup>8</sup> are each independently a hydrogen atom, an alkyl, aralkyl, aryl, or cycloalkyl group; X<sup>1</sup> and X<sup>2</sup> are each independently a hydrogen atom, an alkyl, aralkyl, aryl, or cycloalkyl group; Y is a single bond, an alkyl, alkylene, cycloalkyl, aryl, or aralkyl chain; a repetition number p is an integer of 1 to 3.



20 wherein Ar<sup>8</sup> to Ar<sup>11</sup> are each independently an aryl group having 6 to 50 nucleus carbon atoms which may be substituted with an alkyl, alkoxy or aryl group; Ar<sup>8</sup> and Ar<sup>9</sup>, or Ar<sup>10</sup> and Ar<sup>11</sup> may be connected to each other through a single bond or through O, S or substituted or non-substituted alkylene as a connecting group; and R<sup>9</sup> is an alkyl or alkoxy group, or a substituted or non-substituted aryl group having 6 to 18 nucleus carbon atoms.



35 wherein Z is a trivalent nitrogen atom or an aromatic group; Ar<sup>12</sup> to Ar<sup>14</sup> are each independently a group represented by the following general formula (5) or an aryl group having 6 to 50 nucleus carbon atoms; and at least two of Ar<sup>12</sup> to Ar<sup>14</sup> are groups represented by the following general formula (5):



wherein  $R^{10}$  to  $R^{21}$  are each independently an aryl group having 6 to 50 nucleus carbon atoms which may be substituted with an alkyl, alkoxy group having 1 to 6 carbon atoms, or a phenyl group; and groups adjacent to each other may form a cyclic structure; and a repetition number  $q$  is an integer of 0 to 3.

The organic EL element wherein this carbazole derivative is used as a host material in the organic luminescence layer makes it possible to use the triplet exciton state more effectively, and has a practical life span.

[3] In the organic EL element of the present invention, it is preferred that the carbazole derivative has at least two carbazole skeletons.

This carbazole derivative has a large triplet energy to make it possible to use the triplet exciton state more effectively even at room temperature (20°C), and has a practical life span.

[4] In the organic EL element of the present invention, it is preferred that the relationship of  $E1 > E2$  is satisfied in which  $E1$  represents the triplet energy of the carbazole derivative and  $E2$  represents the triplet energy of the phosphorescent dopant.

This structure makes it possible to transfer the triplet energy of the carbazole derivative surely to the phosphorescent dopant, and to emit fluorescence using the triplet energy even at room temperature (20°C).

[5] In the organic EL element of the present invention, it is preferred that the triplet energy ( $E1$ ) of the carbazole derivative is a value of 21,000  $\text{cm}^{-1}$  or more.

A triplet energy of 21,000  $\text{cm}^{-1}$  corresponds to a light wavelength of 488 nm. On the contrary, various phosphorescent dopants generally have a triplet energy which is equal to or less than the energy which 488 nm light has. Therefore, by using the carbazole derivative having such a large triplet energy as above, various phosphorescent dopants can be used.

Thus, by selecting an appropriate kind of the phosphorescent dopant for the carbazole derivative having such a large triplet energy as above, luminescence in green, yellow, orange, vermillion, red and the like can easily be obtained.

[6] In the organic EL element of the present invention, it is preferred that the carbazole derivative has a cyclic structure whose triplet energy is a value of  $21,000 \text{ cm}^{-1}$  or more, and the cyclic structure contains an aromatic ring, a hetero ring, or combination thereof.

This carbazole derivative makes it possible to transfer the triplet energy of the carbazole derivative more effectively to the phosphorescent dopant. Specifically, if the carbazole derivative has a cyclic structure having a triplet energy of less than  $21,000 \text{ cm}^{-1}$ , the triplet energy is transferred to this cyclic structure so that the triplet energy transferred to the phosphorescent dopant may be reduced.

[7] In the organic EL element of the present invention, it is preferred that the phosphorescent dopant is a metal complex comprising at least one metal selected from the group consisting of Ir (iridium), Ru (ruthenium), Pd (palladium), Pt (platinum), Os (osmium) and Re (rhenium).

This structure makes it possible to transfer energy effectively from the triplet exciton of the carbazole derivative as a host material to the metal complex as the phosphorescent dopant.

[8] In the organic EL element of the present invention, it is preferred that at least one ligand of the metal complex has at least one skeleton selected from the group consisting of phenylpyridine, bipyridyl and phenanthroline skeletons.

The bulky and electron-withdrawing skeleton(s) contained in the molecule makes it possible to transfer energy effectively from the triplet exciton of the carbazole derivative to the metal complex.

[9] In the organic EL element of the present invention, it is preferred that a blend amount of the phosphorescent dopant is 0.1 to 30 parts by weight per 100 parts of the carbazole derivative.

This structure makes it possible to mix the phosphorescent dopant with the carbazole derivative uniformly, and transfer energy effectively from the triplet exciton of the carbazole derivative to the phosphorescent dopant.

[10] In the organic EL element of the present invention, it is preferred that a hole barrier layer, an electron injection layer, or combination thereof is arranged between the anode layer and the cathode layer, and the hole barrier layer and the electron injection layer comprise an alkali metal.

[0016] This structure makes it possible to drive the organic EL element at a lower voltage, and make the life span of the element longer.

## BRIEF DESCRIPTION OF THE DRAWING

[0017] FIG. 1 is a view illustrating a basic structure of an organic EL element.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0018] Referring to FIG. 1, embodiments of the organic EL elements of the present invention will be described. FIG. 1 is a sectional view of an organic EL element 102, and illustrates a structure wherein an anode layer 10, an organic luminescence layer 14 and a cathode layer 16 are successively deposited on a substrate 18.

[0019] The following will chiefly describe a carbazole derivative (host material) and a phosphorescent dopant that constitute the organic luminescence layer 14, which is a characteristic element in the present embodiment. Thus, the structure and the production process of the other elements, for example, the anode layer 10 and the cathode layer 16 will briefly be described. For elements which are not referred to, structures and production processes which are generally known in the field of organic EL elements can be adopted.

### 1. Carbazole derivative

#### (1) Kind 1

[0020] An embodiment of the present invention is characterized in that in the organic luminescence layer, a carbazole derivative with a glass-transition temperature of  $110^\circ\text{C}$  or higher is used as a host material.

[0021] This is because if the host material is a carbazole derivative, the triplet exciton state of the carbazole derivative can be effectively used even at room temperature ( $20^\circ\text{C}$ ) by combining the derivative with a phosphorescent dopant that will be described later. Specifically, a luminescence phenomenon can be caused by transferring energy effectively from the triplet state in the carbazole derivative to the phosphorescent dopant.

[0022] Such a carbazole derivative is preferably a carbazole derivative having at least two carbazole skeletons. This is because the glass-transition temperature and triplet energy that will be described later can easily be adjusted and the derivative can easily be mixed with the phosphorescent dopant.

[0023] The reason why the carbazole derivative having a glass-transition temperature of  $110^\circ\text{C}$  or higher is used is as follows. If the glass-transition temperature is below  $110^\circ\text{C}$ , any combination thereof with the phosphorescent dopant

is very easily crystallized so that the life becomes short. If the glass-transition temperature is below 110°C, a short circuit is easily caused in a short time when an electric current is passed through the derivative at a high temperature. Thus, the environment where the organic element EL is used is excessively restricted.

[0024] Therefore, the glass-transition temperature of the carbazole derivative is more preferably from 115 to 170°C, and still more preferably from 120 to 150°C.

[0025] The reason why the glass-transition temperature of the carbazole derivative is more preferably 170°C or lower is that the kinds of carbazole derivatives having a glass-transition over 170°C are excessively restricted and the handling of the derivatives becomes difficult because of a drop in their deposition ability.

[0026] A Differential Scanning Calorimeter (DSC) is used to make it possible to obtain the glass-transition temperature (T<sub>g</sub>) of the carbazole derivative as a temperature of a change in the specific heat obtained when the derivative is heated at a temperature-rising rate of, for example, 10°C/minute in a nitrogen-circulating state.

## (2) Kind 2

[0027] In the embodiment of the present invention, it is preferred that the relationship of E1 > E2 is satisfied in which E1 represents the triplet energy of the carbazole derivative in the organic luminescence layer and E2 represents the triplet energy of the phosphorescent dopant therein.

[0028] By combining the carbazole derivative with the phosphorescent dopant with this relationship, the triplet exciton state of the carbazole derivative can surely be used even at room temperature. Specifically other words, a luminescence phenomenon can be caused by transferring energy certainly from the triplet state in the carbazole derivative to the phosphorescent dopant.

[0029] It is also preferred that the triplet energy (E1) of the carbazole derivative is set to a value of 21,000 cm<sup>-1</sup> or more.

[0030] Specifically, the triplet energy, 21,000 cm<sup>-1</sup> corresponds to a light wavelength of 488 nm. In general, various phosphorescent dopants have a triplet energy which is equal to or less than the energy which 488 nm light has. Therefore, one or more selected from various phosphorescent dopants can be combined with the carbazole derivative.

[0031] Thus, by selecting the kind of the phosphorescent dopant appropriately, luminescence in green, yellow, orange, vermilion, red and the like can be obtained.

[0032] Moreover, by setting the triplet energy (E1) of the carbazole derivative to a value of 22,500 cm<sup>-1</sup> or more, luminescence in blue also can be obtained easily.

[0033] Preferably, the carbazole derivative has a cyclic structure whose triplet energy is a value of 21,000 cm<sup>-1</sup> or more and the cyclic structure contains an aromatic ring, a hetero ring, or combination one thereof.

[0034] If the carbazole derivative has such a cyclic structure, the triplet exciton state of the carbazole derivative can be effectively used even at room temperature by combining the carbazole derivative with the phosphorescent dopant. That is, by causing the carbazole derivative to have, for example, a cyclic structure wherein 9-arylcarbazole is connected to a bivalent or trivalent group consisting an aromatic ring, the triplet energy can be set to 22,500 cm<sup>-1</sup> or less. Therefore, if the carbazole derivative has such a cyclic structure, the frequency that the triplet energy of 21,000 cm, originating from the carbazole group, is transferred in the molecule becomes small. Thus, the triplet energy which is transferred to the phosphorescent dopant becomes relatively large.

## (3) Kind 3

[0035] It is preferred to use, as the above-mentioned carbazole derivative, carbazole derivatives represented by the general formulae (1) to (4) alone or in combination of two or more.

[0036] In the general formulae (1) to (4) representing preferred carbazole derivatives, examples of preferred aryl groups having 5 to 50 nucleus atoms include phenyl, naphthyl, anthranyl, phenanthryl, pyrenyl, coronyl, biphenyl, terphenyl, pyrrolyl, furanyl, thiophenyl, benzothiofenyl, oxadiazolyl, diphenylanthranlyl, indolyl, carbazoly, pyridyl, and benzoquinolyl, and the like.

[0037] Examples of preferred arylene groups having 5 to 50 nucleus atoms include phenylene, naphthylene, anthra-nylene, phenanthrylene, pyrenylene, coronylene, biphenylene, terphenylene, pyrrolylene, furanylene, thiophenylene, benzothiofenylene, oxadiazolyene, diphenylanthranylene, indolyene, carbazolyene, pyridylene, and benzoquinolyene, and the like.

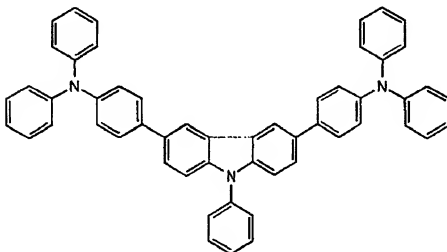
[0038] The aromatic group having 6 to 50 carbon atoms may be substituted with one or more substituents. Preferred examples of the substituent include alkyl groups having 1 to 6 carbon atoms (such as methyl, ethyl, i-propyl, n-propyl, s-butyl, t-butyl, pentyl, hexyl, cyclopentyl and cyclohexyl groups); alkoxy groups having 1-6 carbon atoms (such as methoxy, ethoxy, i-propoxy, n-propoxy, s-butoxy, t-butoxy, pentoxy, hexyloxy, cyclopentoxy and cyclohexyloxy groups); aryl groups having 5 to 50 nucleus atoms; amino groups substituted with an aryl group having 5 to 50 nucleus atoms; ester groups having an aryl group having 5 to 50 nucleus atoms; ester groups having an alkyl group having 1 to 6 carbon atoms; a cyano group; a nitro group; halogen atoms. The above-mentioned substituent may be substituted with



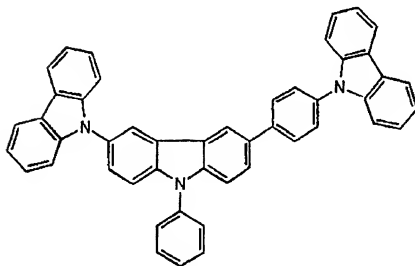
a carbazolyl group.

**[0039]** Moreover, as shown in the general formulae (1) and (3) described below, the carbazole in the present invention is interpreted as a moiety formed by connecting at least two aryl groups, each of which is connected to a nitrogen atom, to each other through a single bond or a connecting groups. In this case, preferred examples of the connecting groups include O, S, and substituted or non-substituted alkylene and silylene, and the like.

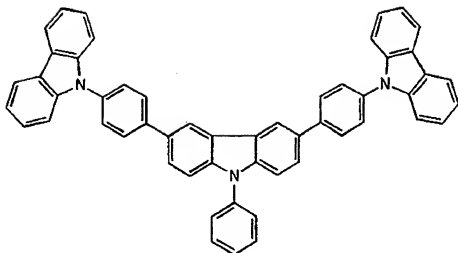
**[0040]** Here, preferred specific examples of the carbazole derivative represented by the formula (1) include a group of compounds illustrated as the following chemical formulae (7) to (24).



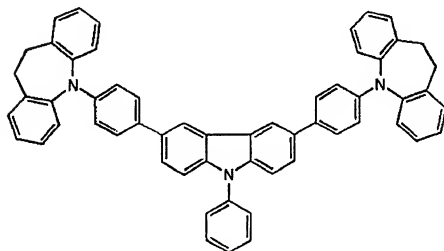
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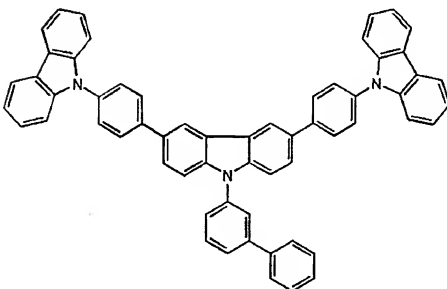
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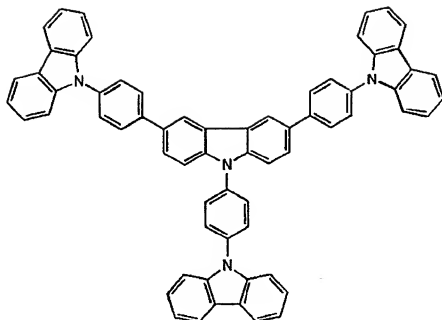
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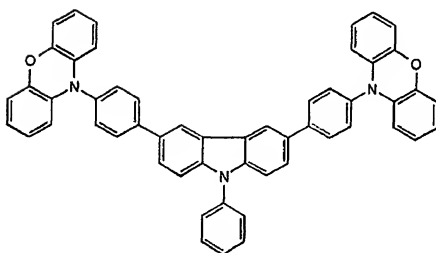
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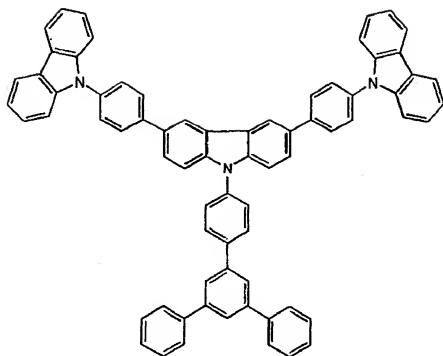
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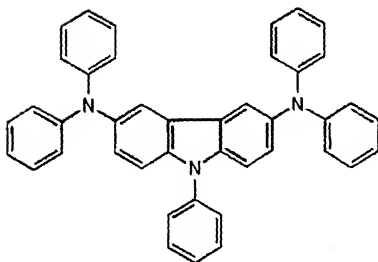
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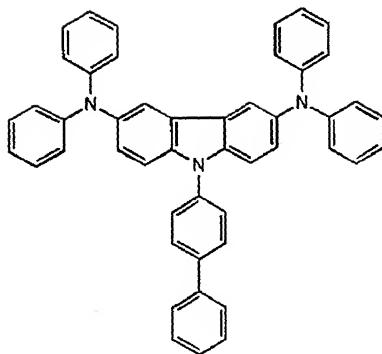
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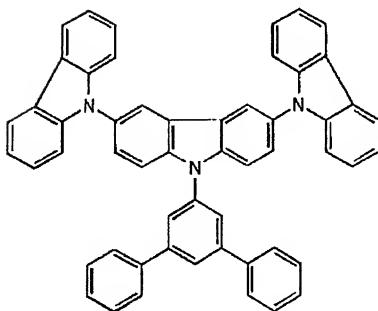
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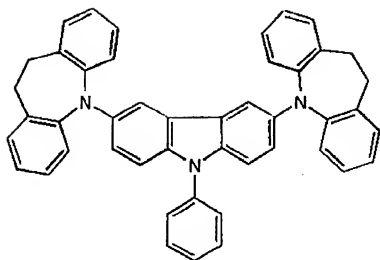
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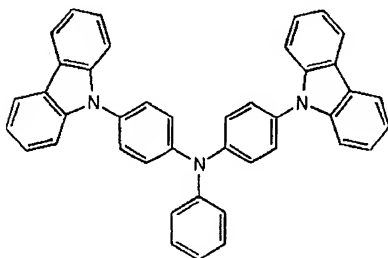
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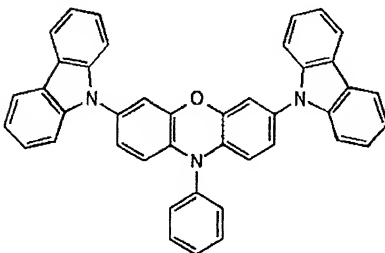
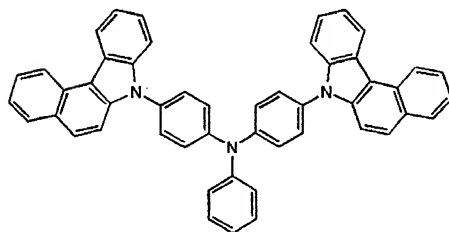
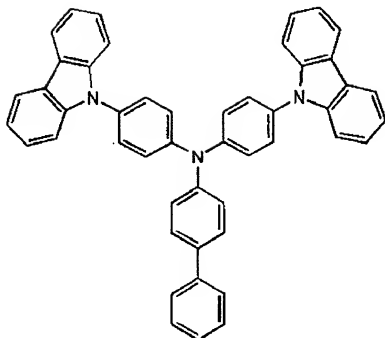
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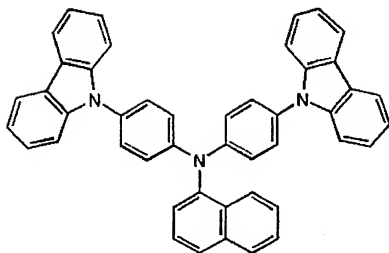


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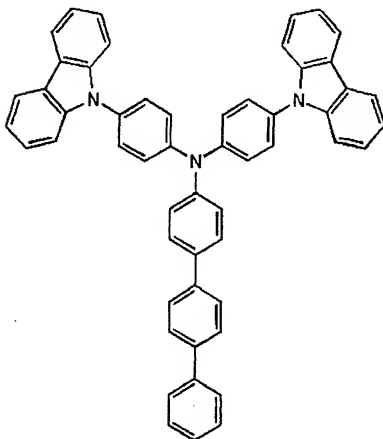


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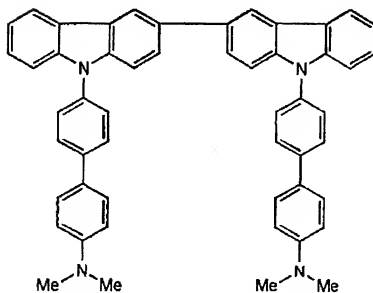
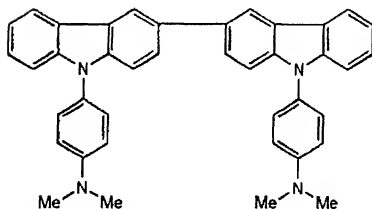
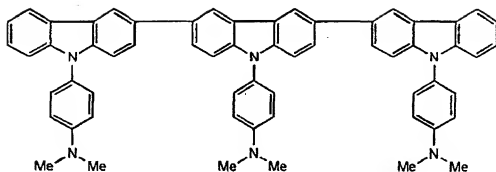
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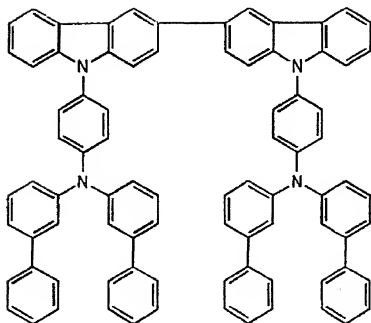


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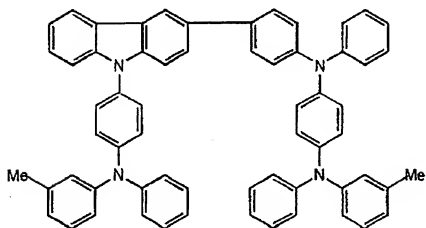
[0041] Preferred specific examples of the carbazole derivative represented by the formula (2) include a group of compounds illustrated as the following chemical formulae (25) to (29). In the formula, a methyl group may be abbreviated to Me.





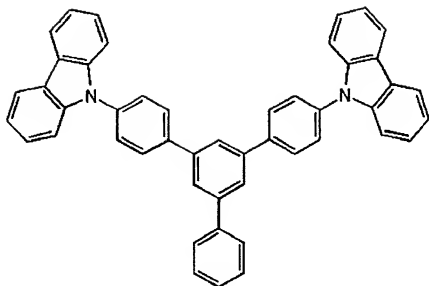


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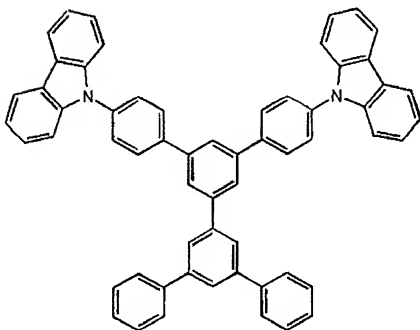


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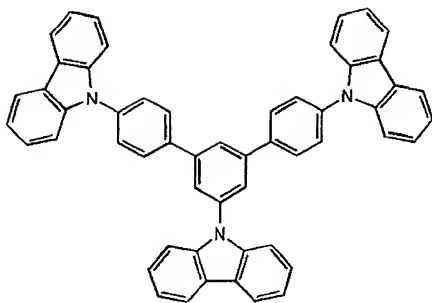
[0042] Preferred specific examples of the carbazole derivative represented by the formula (3) include a group of compounds illustrated as the following chemical formulae (30) to (41).



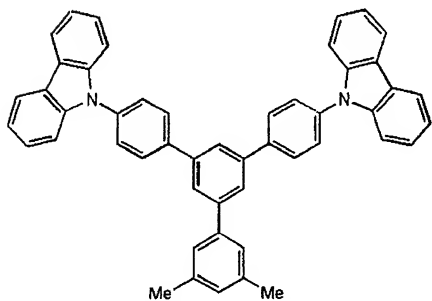
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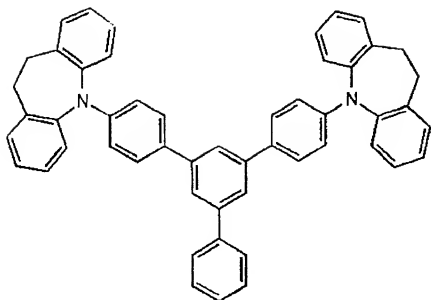
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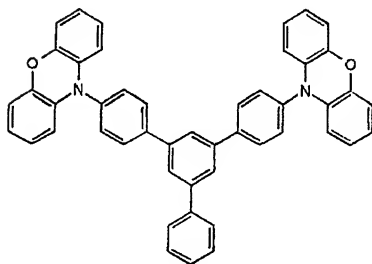
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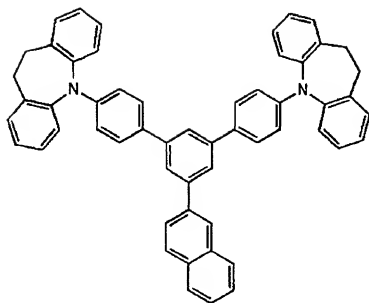
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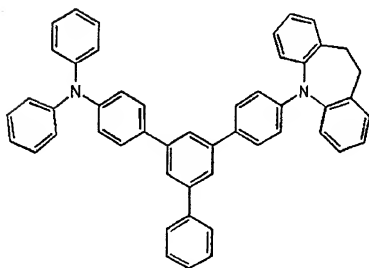
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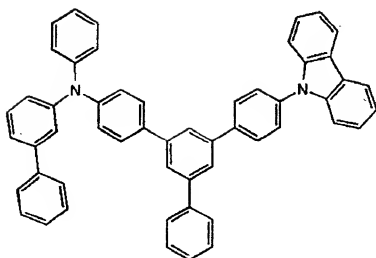
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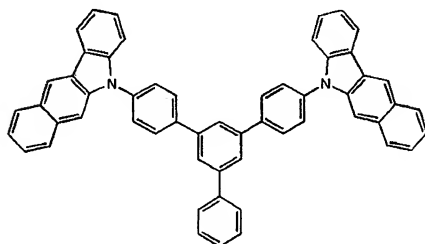
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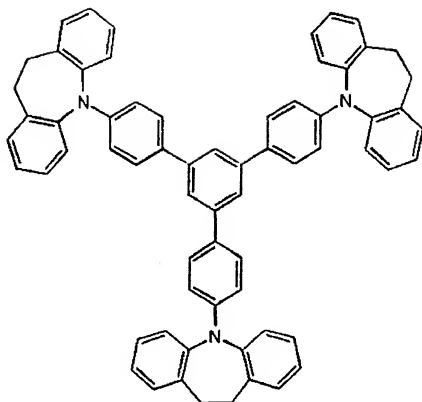
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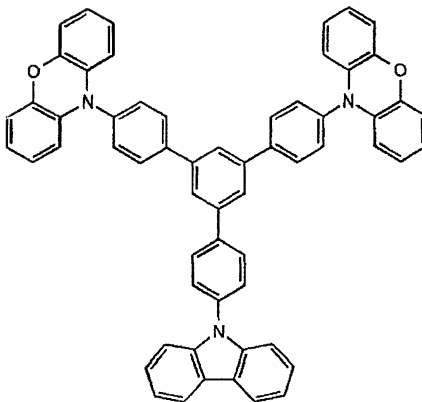
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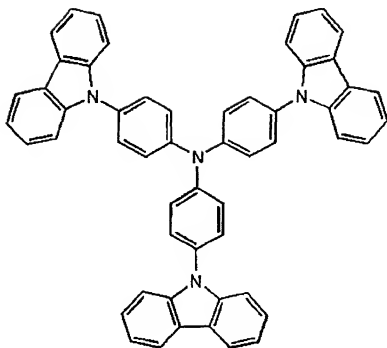
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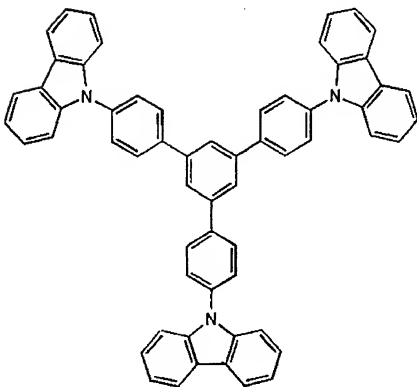
(41)

[0043] Preferred specific examples of the carbazole derivative represented by the formula (4) include a group of compounds illustrated as the following chemical formulae (42) to (49).

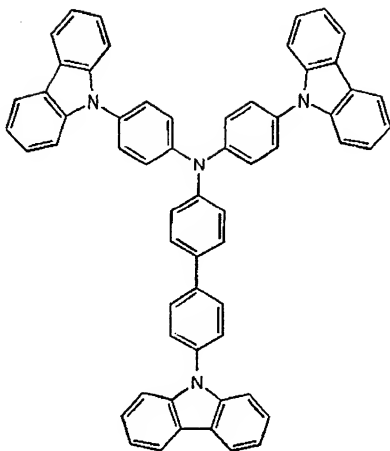




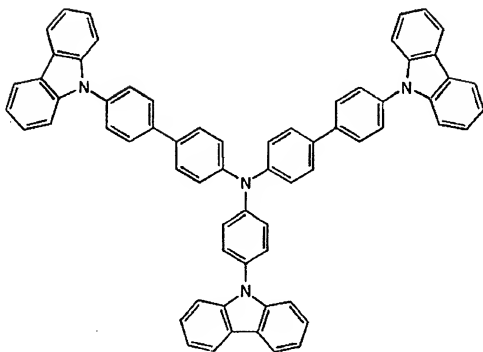
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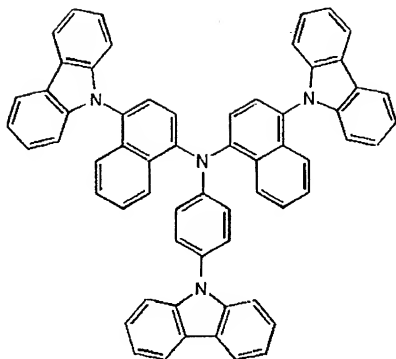
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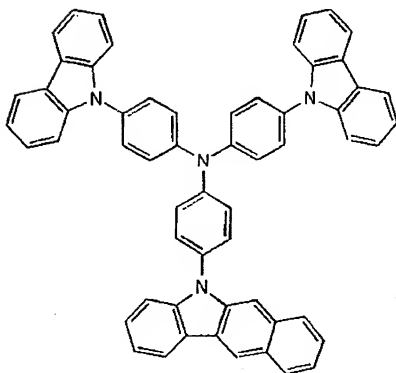
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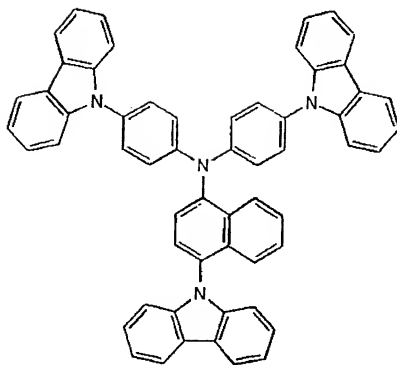
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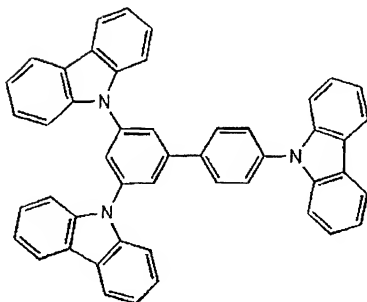
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(47)

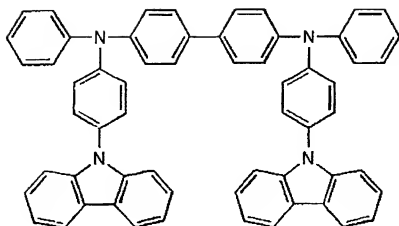


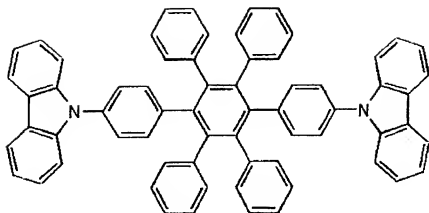
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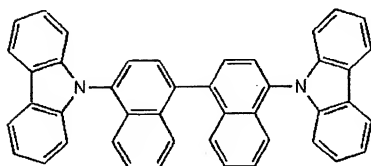
(49)

[0044] Furthermore, specific examples of the carbazole derivative having a structure other than the structures represented by the general formulae (1) to (4) include a group of compounds illustrated as the following chemical formulae (50) to (59).

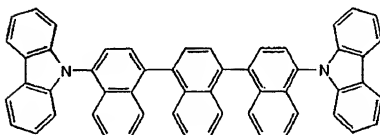




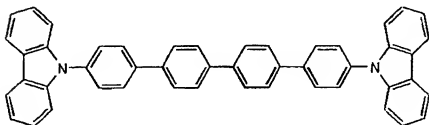
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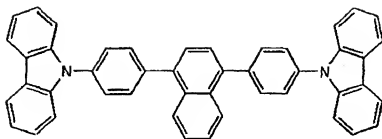
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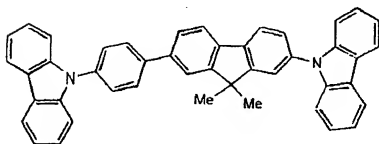
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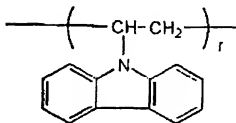
(56)



(57)



(58)



(59)

wherein a repetition number is an integer of 3 to 20.

## 2. Phosphorescent dopant

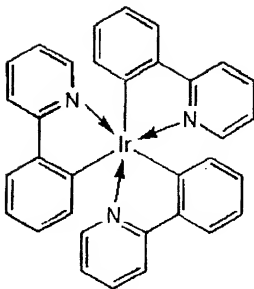
### (1) Kind

#### ① Metal complex

**[0045]** The phosphorescent dopant is preferably a metal complex comprising at least one metal selected from the group consisting of Ir, Ru, Pd, Pt, Os and Re.

**[0046]** This is because if the phosphorescent dopant is any one of these metal complexes, energy can be effectively transferred from triplet excitons of the carbazole derivative as a host material to the phosphorescent dopant.

**[0047]** More specific examples of the phosphorescent dopant are metal complexes such as tris(2-phenylpyridine) iridium, tris(2-phenylpyridine) ruthenium, tris(2-phenylpyridine) palladium, bis(2-phenylpyridine) platinum, tris(2-phenylpyridine) osmium, tris(2-phenylpyridine) rhenium, octaethyl platinum porphyrin, octaphenyl platinum porphyrin, octaethyl palladium porphyrin, and octaphenyl palladium porphyrin. In order to transfer energy more effectively to emit fluorescence, more preferred are metal complexes comprising Ir, for example, tris(2-phenylpyridine) iridium represented by the following formula (60):



(60)

② Ligand of the metal complex

[0048] At least one ligand of the metal complex preferably has at least one skeleton selected from the group consisting of phenylpyridine, bipyridyl and phenanthroline skeletons.

[0049] This is because by at least one of these electron withdrawing skeletons contained in the molecule, energy can be effectively transferred from the triplet excitons of the carbazole derivative to the metal complex.

[0050] Particularly, in the phosphorescent dopant, the ligand preferably has a phenylpyridine skeleton among these skeletons, such as tris(2-phenylpyridine) iridium. (2) Added amount

[0051] A blend amount of the phosphorescent dopant is preferably 0.1 to 30 parts by weight per 100 parts by weight of the blended carbazole derivative (host material).

[0052] The reasons for this are as follows. If the blend amount of the phosphorescent dopant is below 0.1 part by weight, the effect based on the blend is not exhibited so that energy may not be effectively transferred from triplet excitons of the carbazole derivative. On the other hand, if the blend amount of the phosphorescent dopant is over 30 parts by weight, the phosphorescent dopant is not easily blended with the carbazole derivative uniformly so that luminescence brightness may be scattered.

[0053] Therefore, the blend amount of the phosphorescent dopant is more preferably 0.5 to 20 parts by weight, and is still more preferably 1 to 15 parts by weight.

### 3. Other organic layers in the organic luminescence medium

#### (1) Hole injection layer

[0054] It is preferred to deposit a hole injection layer having a thickness of 5 nm to 5  $\mu$ m. The deposition of such a hole injection layer makes it possible to inject holes satisfactorily into the organic luminescence layer, give a high luminescence brightness, and attain driving at a low voltage.

[0055] It is also preferred to use, in the hole injection layer in the organic luminescence medium, a compound having a hole mobility of  $1 \times 10^{-6}$  cm<sup>2</sup>/V-second or more and an ionization energy of 5.5 eV or less. The hole mobility is measured when a voltage of  $1 \times 10^4$  to  $1 \times 10^6$  V/cm is applied to the hole injection layer.

[0056] Specific examples of the constituent material of the hole injection layer are organic compounds such as porphyrin compounds, aromatic tertiary amine compounds, styrylamine compounds, aromatic dimethyldiene compounds, and condensed aromatic ring compounds, for example, 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (abbreviated to NPD) and 4,4'-bis[N-(3-methylphenyl)-N-phenylamino]triphenylamine (abbreviated to MTDATA).

[0057] As the constituent material of the hole injection layer, an inorganic compound such as p-type Si or p-type SiC is preferably used.

[0058] It is also preferred to arrange an organic semiconductor layer having an electric conductivity of  $1 \times 10^{-10}$  S/cm or more between the hole injection layer and the anode layer, or between the hole injection layer and the organic luminescence layer. The arrangement of the organic semiconductor layer makes the injection of holes into the organic luminescence layer more satisfactory. (2) Electron injection layer



[0059] It is preferred to deposit an electron injection layer having a thickness of 5 nm to 5  $\mu\text{m}$ . The deposition of such an electron injection layer makes it possible to inject electrons satisfactorily into the organic luminescence layer, give a high luminescence brightness, and attain driving at a low voltage.

[0060] It is also preferred to use, in the electron injection layer, a compound having an electron mobility of  $1 \times 10^{-6} \text{ cm}^2/\text{V}\cdot\text{second}$  or more and an ionization energy over 5.5 eV. The electron mobility is measured when a voltage of  $1 \times 10^4$  to  $1 \times 10^6 \text{ V/cm}$  is applied to the electron injection layer.

[0061] Specific examples of the constituent material of the electron injection layer are metal complexes of 8-hydroxyquinoline (Alq), derivatives thereof, and oxadiazole derivatives.

[0062] If an alkali metal is incorporated into the electron injection layer in the same way as into a hole barrier layer that will be described later, the organic EL element can be driven at a notably low voltage and the life thereof can be made longer.

### (3) Hole barrier layer

[0063] It is preferred to arrange a hole barrier layer having a thickness of 5 nm to 5  $\mu\text{m}$  between the organic luminescence layer and the cathode. The arrangement of the hole barrier layer makes it possible to improve capability of confining holes in the organic luminescence layer, give a high luminescence brightness, and attain driving at a low voltage.

[0064] Examples of the constituent material of the hole barrier layer include 2,9-diethyl-4,7-diphenyl-1,10-phenanthroline and 2,9-diethyl-4,7-diphenyl-1,10-phenanthroline, and the like. More preferably, an alkali metal such as Li or Cs is further added thereto.

[0065] The combination of the alkali metal with the hole barrier layer constituting material in the hole barrier layer makes it possible to drive the organic EL element at a notably low voltage and make the life thereof longer.

[0066] When the alkali metal is incorporated, the amount thereof is preferably 0.01 to 30 % by weight. (if the total amount of the hole barrier layer is 100 % by weight)

[0067] If the amount of the alkali metal is below 0.01 % by weight, the effect of the addition thereof may be not exhibited. On the other hand, if the amount is over 30 % by weight, the dispersion of the alkali metal becomes uneven so that luminescence brightness may be scattered.

[0068] Therefore, the amount of the alkali metal is more preferably 0.05 to 20 % by weight, and more still preferably 0.1 to 15 % by weight.

## 4. Electrode

### (1) Anode layer

[0069] The anode layer corresponds to a lower electrode or an opposite electrode, dependently on the structure of the organic EL display device. The anode layer is preferably made of a metal, an alloy or an electrically conductive compound having a large work function (for example, 4.0 eV or more), or a mixture thereof. Specifically, it is preferred to use one or a combination of two or more electrode materials selected from indium tin oxide (ITO), indium zinc oxide (IZO), copper iodide (CuI), tin oxide ( $\text{SnO}_2$ ), zinc oxide ( $\text{ZnO}$ ), gold, platinum, palladium and the like.

[0070] By using these electrode materials, the anode layer having a uniform thickness can be made using a method making deposition in a dry state possible, such as vacuum evaporation, sputtering, ion plating, electron beam evaporation, CVD (Chemical Vapor Deposition), MOCVD (Metal Oxide Chemical Vapor Deposition), or plasma CVD.

[0071] When EL luminescence is taken out from the anode layer, it is necessary to make the anode layer to a transparent electrode. In this case, it is preferred to use an electrically conductive material such as ITO, IZO, CuI,  $\text{SnO}_2$  or  $\text{ZnO}$  to set the transmissivity of EL luminescence to a value of 70 % or more.

[0072] The thickness of the anode layer is not particularly limited. The thickness is preferably a value of 10 to 1,000 nm, and more preferably a value of 10 to 200 nm.

[0073] If the thickness of the anode layer is set to a value within such a range, uniform thickness distribution can be obtained and the transmissivity of EL luminescence can be made to 70 % or more. Moreover, the sheet resistivity of the anode layer can be made to a value of  $1000 \Omega/\square$  or less, and preferably  $100 \Omega/\square$  or less.

[0074] It is also preferred that light is emitted from an arbitrary pixel in the luminescence face by depositing the anode layer (lower electrode), the organic luminescence medium, and the cathode layer (opposite electrode) successively and making the lower electrode and the opposite electrode into an XY matrix pattern. By making the anode and so on into this manner, various data can easily be displayed in the organic EL element.

## (2) Cathode layer

[0075] The cathode layer also corresponds to a lower electrode or an opposite electrode, dependently on the structure of the organic EL display device. The cathode layer is preferably made of a metal, an alloy or an electrically conductive compound having a small work function (for example, less than 4.0 eV), or a mixture thereof.

[0076] Specifically, it is preferred to use any one or a combination of two or more electrode materials selected from sodium, sodium-potassium alloy, cesium, magnesium, lithium, magnesium-silver alloy, aluminum, aluminum oxide, aluminum-lithium alloy, indium, a rare earth metal, a mixture of an organic luminescence medium material and these metals, a mixture of an electron injection layer material and these metals, and the like.

[0077] The thickness of the cathode layer is not particularly limited. The thickness is preferably a value of 10 to 1,000 nm, and more preferably a value of 10 to 200 nm.

[0078] Furthermore, when EL luminescence is taken out from the cathode layer, it is necessary to make the cathode layer to a transparent electrode. In this case, it is preferred to set the transmissivity of EL luminescence to a value of 70 % or more.

[0079] The cathode layer is preferably formed by a method making deposition in a dry state possible, such as vacuum evaporation or sputtering, in the same way as for the anode layer.

## 5. Supporting substrate

[0080] The supporting substrate in the organic EL element is preferably a substrate which has superior mechanical strength and small permeability of moisture or oxygen. Specific examples thereof include glass plates, metal plates, ceramic plates and plastic plates (such as polycarbonate resin, acrylic resin, vinyl chloride resin, polyethylene terephthalate resin, polyimide resin, polyester resin, epoxy resin, phenol resin, silicone resin, and fluorine resin plates) and the like.

[0081] To avoid invasion of moisture into the organic EL element, it is preferred to form an inorganic film or apply a fluorine resin onto the supporting substrate made of such a material as above to conduct moisture-proof treatment or hydrophobic treatment.

[0082] Particularly to avoid invasion of moisture into the organic luminescence medium, it is preferred to make the water content in the supporting substrate and the gas transmissivity thereof small. Specifically, it is preferred to set the water content in the supporting substrate to 0.0001 % or less by weight and set the gas transmissivity thereof to  $1 \times 10^{-13}$  cc/cm<sup>2</sup>·sec. cmHg or less.

## Example

## [Example 1]

## (Production of an organic EL element)

## ① Washing

[0083] A glass substrate (made by Geomatic company) 25 mm in width, 75 mm in length and 1.1 mm in thickness, with ITO transparent electrodes, was subjected to ultrasonic washing in isopropyl alcohol for 5 minutes and subjected to UV ozone washing for 30 minutes.

## ② Formation of a hole injection layer

[0084] The washed glass substrate with the ITO transparent electrodes was set to a substrate holder in a vacuum evaporation device, and then N,N-bis(N,N-diphenyl-4-aminophenyl)-N,N-diphenyl-4,4'-diamino-1,1'-biphenyl (abbreviated to TPD232 hereinafter) was vapor-deposited on the substrate at a vacuum degree of  $665 \times 10^{-7}$  Pa and a vapor-deposition rate of 0.1 to 0.3 nm/sec., so as to form a first hole injection layer (which also had a function as a hole transport layer) having a thickness of 60 nm.

[0085] 4,4-Bis[N-(1-naphthyl)-N-phenylamino]biphenyl (abbreviated to NPD hereinafter) was vapor-deposited on the TPD232 film at a vacuum degree of  $665 \times 10^{-7}$  Pa and a vapor-deposition rate of 0.1 to 0.3 nm/sec., so as to form a second hole injection layer (which also had a function as a hole transport layer) having a thickness of 20 nm.

## ③ Formation of an organic luminescence layer

[0086] Next, the same vacuum evaporation device was used to vapor-deposit a carbazole compound (T<sub>g</sub>: 110°C or

higher) represented by the formula (9) on the NPD film formed in the previous step at a vacuum degree of  $665 \times 10^{-7}$  Pa and a vapor-deposition rate of 0.1 to 0.3 nm/sec., so as to form an organic luminescence layer having a thickness of 30 nm.

[0087] In this case, at the same time of the vapor deposition of the carbazole derivative compound represented by the formula (9), tris(2-phenylpyridine) iridium was vapor-deposited as a phosphorescent dopant. In this vapor co-deposition, the vapor-deposition rate of the phosphorescent dopant was adjusted in the manner that the ratio of the amount of the blended phosphorescent dopant to the total amount of the organic luminescence layer would be 7 % by weight. (if the total amount of the organic luminescence layer is 100 % by weight)

#### ④ Formation of a hole barrier layer

[0088] Next, the same vacuum evaporation device was used to vapor-deposit 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (abbreviated to BCP hereinafter) on the organic luminescence layer formed in the previous step at a vacuum degree of  $665 \times 10^{-7}$  Pa and a vapor-deposition rate of 0.1 to 0.3 nm/sec., so as to form an organic luminescence layer having a thickness of 10 nm.

#### ⑤ Formation of an electron injection layer

[0089] Next, the same vacuum evaporation device was used to deposit a tris(8-quinolinol) aluminum film (abbreviated to Alq film hereinafter) on the hole barrier layer formed in the previous step at a vacuum degree of  $665 \times 10^{-7}$  Pa and a vapor-deposition rate of 0.1 to 0.3 nm/sec., so as to form an electron injection layer.

[0090] At this time, Li (Li source made by Saesu getter company) and Alq were subjected to vapor co-deposition in the manner that the molar ratio between them would be 1:1, so that the electron injection layer was made to an Alq/Li film having a thickness of 20 nm.

#### ⑥ Formation of a cathode

[0091] Next, the same vacuum evaporation device was used to vapor-deposit metal Al on the electron injection layer formed in the previous step at a vacuum degree of  $665 \times 10^{-7}$  Pa and a vapor-deposition rate of 0.5 to 1.0 nm/sec., so as to form a cathode having a thickness of 150 nm.

#### ⑦ Sealing step

[0092] The resultant organic EL element was put into a dry box into which nitrogen was introduced. Furthermore, its luminescence face was coated with blue glass and the periphery thereof was treated with a cation-setting adhesive TB3102 (made by Three Bond Co., Ltd.) to perform sealing.

[0093] In this way, the organic EL element of Example 1 was prepared.

#### (Evaluation of the organic EL element)

[0094] A DC voltage of 6 V was applied between the anode and the cathode in the resultant organic EL element, so that green luminescence having a luminescence brightness of 1,200 cd/m<sup>2</sup> and a luminescence efficiency of 40 cd/A was obtained.

[0095] The organic EL element was driven at a low voltage. The initial brightness thereof was set to 500 cd/m<sup>2</sup>. In this way, a life span test was performed. As a result, the half-time, which is a driving time until the initial brightness becomes half, was 500 hours. This half-time is practical.

[0096] A current-sending test as a heat-resistance test was performed at 85°C. Even after current was sent for 200 hours, green luminescence having sufficient luminescence brightness was obtained.

[0097] The obtained results are shown in Table 1.

#### [Example 2]

[0098] An organic EL element was produced and evaluated in the same way as in Example 1 except that at the time of vapor-depositing BCP for the hole barrier layer in Example 1, metal Li, which is an alkali metal, and BCP were subjected to vapor co-deposition at a molar ratio of 1:1.

[0099] As a result, even by application of a DC voltage of 5 V, green luminescence having a luminescence brightness of 1,300 cd/m<sup>2</sup> and a luminescence efficiency of 37 cd/A was obtained.

[0100] The organic EL element was driven at a low voltage. The initial brightness thereof was set to 500 cd/m<sup>2</sup>. In

this way, a life span test was performed, so that the half-time was 700 hours.

[0101] A current-sending test as a heat-resistance test was performed at 85°C. Even after current was sent for 200 hours, green luminescence having sufficient luminescence brightness was obtained.

[Example 3]

[0102] An organic EL element was produced and evaluated in the same way as in Example 1 except that at the time of vapor-depositing BCP for the hole barrier layer in Example 1, metal Cs, which is an alkali metal, and BCP were subjected to vapor co-deposition at a molar ratio of 1:1.

[0103] As a result, even by application of a DC voltage of 4.5 V, green luminescence having a luminescence brightness of 1,200 cd/m<sup>2</sup> and a luminescence efficiency of 40 cd/A was obtained.

[0104] The organic EL element was driven at a low voltage. The initial brightness thereof was set to 500 cd/m<sup>2</sup>. In this way, a life span test was performed, so that the half-time was 800 hours.

[0105] A current-sending test as a heat-resistance test was performed at 85°C. Even after current was sent for 200 hours, green luminescence having sufficient luminescence brightness was obtained.

[Comparative Example 1]

[0106] An organic EL element was produced and evaluated in the same way as in Example 1 except that instead of the carbazole compound represented by the formula (9), a carbazole compound (Tg: less than 110°C) represented by the formula (6) was used in the organic luminescence layer.

[0107] As a result, by application of a DC voltage of 6 V, green luminescence having a luminescence brightness of 1,100 cd/m<sup>2</sup> and a luminescence efficiency of 38 cd/A was obtained.

[0108] The organic EL element was driven at a low voltage. The initial brightness thereof was set to 500 cd/m<sup>2</sup>. In this way, a life span test was performed. However, the half-time was as short as 150 hours. This half-time is not practically allowable.

[0109] A current-sending test as a heat-resistance test was performed at a high temperature of 85°C. A short circuit was caused after 100 hours. The organic EL element was unable to be lighted.

[0110] This demonstrated that the organic EL element of Comparative Example 1 had poor heat-resistance and was unable to be used for car.

Table 1

	Organic luminescence layer Tg (°C)	Hole barrier layer	Voltage (V)	Luminescence brightness (nit)	Luminescence efficiency (cd/A)	Luminescence color
Example 1	Formula (9) > 110	Only BCP	6	1200	40	Green
Example 2	Formula (9) > 110	BCP/Li = 1/1	5	1300	37	Green
Example	3 Formula (9) > 110	BCP/Cs = 1/1	4.5	1200	40	Green
Comparative Example 1	Formula (6) > 110	Only BCP	6	1100	38	Green

[Examples 4 to 9]

**[0111]** An organic EL element was produced and evaluated in the same way as in Example 1 except that instead of the compound represented by the formula (9) of Example 1, each of compounds represented by the formulae (10), (19), (26), (30), (43) and (55) was used as a carbazole compound. The obtained results are shown in Table 2.

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Table 2

	Organic luminescence layer T <sub>g</sub> (°C)	Hole barrier layer	Voltage (V)	Luminescence brightness (nit)	Luminescence efficiency (cd/A)	Luminescence color
Example 4	Formula (10) > 120	Only BCP	6	1050	35	Green
Example 5	Formula (19) > 110	Only BCP	6	600	18	Green
Example 6	Formula (26) > 110	Only BCP	6	450	10	Green
Example 7	Formula (30) > 110	Only BCP	6	890	28	Green
Example 8	Formula (43) > 140	Only BCP	6	920	30	Green
Example 9	Formula (55) > 110	Only BCP	6	350	10	Green

## Industrially Applicability

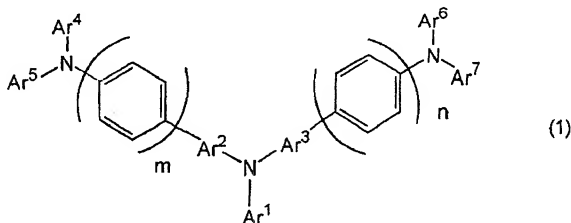
[0112] According to the organic EL element of the present invention, its organic luminescence medium comprises a carbazole derivative with a glass-transition temperature of 110°C or higher, and a phosphorescent dopant, so that the triplet exciton state of the carbazole derivative can be used even at room temperature and this element has a practical life and superior heat-resistance.

## Claims

1. An organic electroluminescence element comprising:

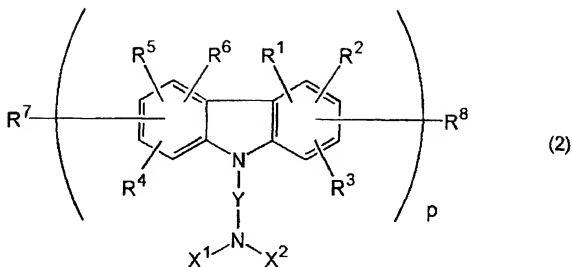
an anode layer,  
a cathode layer, and  
an organic luminescence layer therebetween, the organic luminescence layer having a carbazole derivative with a glass-transition temperature of 110°C or higher, and a phosphorescent dopant.

2. The organic electroluminescence element according to claim 1, wherein the carbazole derivative is at least one of compounds represented by the following general formulae (1) to (4):



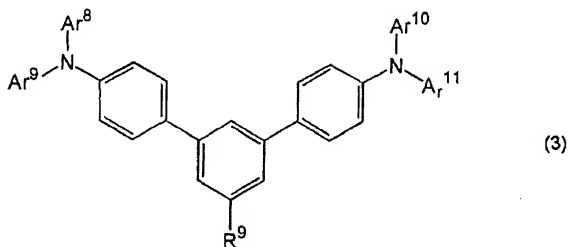
wherein Ar¹ is a substituted or non-substituted aryl group having 6 to 50 nucleus carbon atoms; Ar² to Ar⁷ are each independently a substituted or non-substituted aryl or arylene group having 6 to 50 nucleus carbon atoms; Ar² and Ar³, Ar⁴ and Ar⁵, or Ar⁶ and Ar⁷ may be connected to each other through a single bond or through O, S or substituted or non-substituted alkylene as a connecting group; and each of repetition numbers m and n is an integer of 0 to 3,





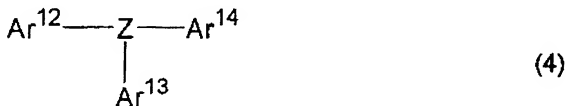
20 wherein R<sup>1</sup> to R<sup>6</sup> are each independently a hydrogen or halogen atom, an alkyl, aralkyl, aryl, cycloalkyl, fluoroalkyl, amino, nitro, cyano, hydroxy, or alkoxy group; R<sup>7</sup> and R<sup>8</sup> are each independently a hydrogen atom, an alkyl, aralkyl, aryl, or cycloalkyl group; X<sup>1</sup> and X<sup>2</sup> are each independently a hydrogen atom, an alkyl, aralkyl, aryl, or cycloalkyl group; Y is a single bond, an alkyl, alkylene, cycloalkyl, aryl, or aralkyl chain; a repetition number p is an integer of 1 to 3.

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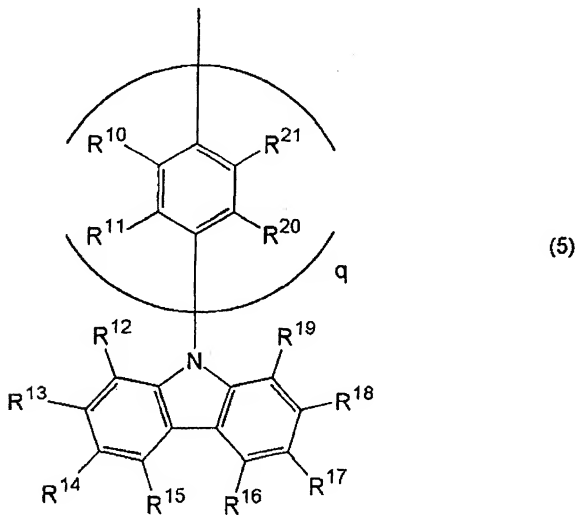


45 wherein Ar<sup>8</sup> to Ar<sup>11</sup> are each independently an aryl group having 6 to 50 nucleus carbon atoms which may be substituted with an alkyl, alkoxy or aryl group; Ar<sup>8</sup> and Ar<sup>9</sup>, or Ar<sup>10</sup> and Ar<sup>11</sup> may be connected to each other through a single bond or through O, S or substituted or non-substituted alkylene as a connecting group; and R<sup>9</sup> is an alkyl or alkoxy group, or a substituted or non-substituted aryl group having 6 to 18 nucleus carbon atoms.

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wherein Z is a trivalent nitrogen atom or an aromatic group; Ar<sup>12</sup> to Ar<sup>14</sup> are each independently a group represented by the following general formula (5) or an aryl group having 6 to 50 nucleus carbon atoms; and at least two of Ar<sup>12</sup> to Ar<sup>14</sup> are groups represented by the following general formula (5):



wherein R<sup>10</sup> to R<sup>21</sup> are each independently an aryl group having 6 to 50 nucleus carbon atoms which may be substituted with an alkyl, alkoxy group having 1 to 6 carbon atoms, or a phenyl group; and groups adjacent to each other may form a cyclic structure; and a repetition number q is an integer of 0 to 3.

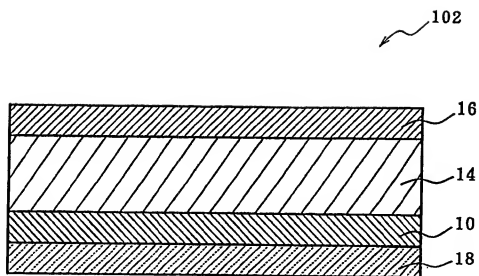
3. The organic electroluminescence element according to claim 1 or 2, wherein the carbazole derivative has at least two carbazole skeletons.
4. The organic electroluminescence element according to any one of claims 1 to 3, wherein relationship of  $E1 > E2$  is satisfied in which E1 represents triplet energy of the carbazole derivative and E2 represents triplet energy of the phosphorescent dopant.
5. The organic electroluminescence element according to any one of claims 1 to 4, wherein triplet energy E1 of the carbazole derivative is a value of 21,000 cm<sup>-1</sup> or more.
6. The organic electroluminescence element according to any one of claims 1 to 5, wherein the carbazole derivative has cyclic structure whose triplet energy is a value of 21,000 cm<sup>-1</sup> or more, and the cyclic structure contains an aromatic ring, a hetero ring, or combination thereof.
7. The organic electroluminescence element according to any one of claims 1 to 6, wherein the phosphorescent

## EP 1 205 527 A1

dopant is a metal complex comprising at least one metal selected from the group consisting of Ir, Ru, Pd, Pt, Os and Re.

8. The organic electroluminescence element according to claim 7, wherein at least one ligand of the metal complex has at least one skeleton selected from the group consisting of phenylpyridine, bipyridyl and phenanthroline skeletons.
9. The organic electroluminescence element according to any one of claims 1 to 8, wherein a blend amount of the phosphorescent dopant is 0.1 to 30 parts by weight per 100 parts of the carbazole derivative.
10. The organic electroluminescence element according to any one of claims 1 to 9, wherein a hole barrier layer, an electron injection layer, or combination thereof is arranged between the anode layer and the cathode layer, and the hole barrier layer and the electron injection layer comprise an alkali metal.

FIG. 1



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP01/02454

A. CLASSIFICATION OF SUBJECT MATTER Int. Cl. <sup>7</sup> C09K11/06, H05B33/14		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int. Cl. <sup>7</sup> C09K11/06, H05B33/14		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) CA (STN), REGISTRY (STN)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	M. A. Baldo et al., "Very high-efficiency green organic light-emitting devices based on electrophosphorescence", Applied Physics Letters, (1999), Vol. 75, No. 1, pages 4 to 6	1-10
X	JP, 2000-63335, A (Minolta Co., Ltd.), 29 February, 2000 (29.02.00), especially, Claims; Par. Nos. [0033] to [0062]; working example 30 (Family: none)	1-6, 9 10
Y	JP, 2000-21572, A (Mitsubishi Chemical Corporation), 21 January, 2000 (21.01.00), especially, Claims; Par. Nos. [0006], [0044], [0048] (Family: none)	1-6, 9 10
Y	JP, 9-298088, A (Mitsubishi Chemical Corporation), 18 November, 1997 (18.11.97), especially, Claims (Family: none)	1-6, 9, 10
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family		
Date of the actual completion of the international search 14 June, 2001 (14.06.01)		Date of mailing of the international search report 26 June, 2001 (26.06.01)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP01/02454

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, 2000-44519, A (Chisso Corporation), 15 February, 2000 (15.02.00), especially, Claims; Par. Nos. [0006], [0020], [0024] (Family: none)	1-10
Y	US, 5891587, A (Xerox Corporation), 06 April, 1999 (06.04.99), & JP, 10-312073, A	1-10
Y	JP, 8-3547, A (Toray Industries, Inc.), 09 January, 1996 (09.01.96), especially, Claims; Par. No. [0009] (Family: none)	1-10
Y	US, 5487953, A (Pioneer Electronic Corporation), 30 January, 1996 (30.01.96), & JP, 7-90256, A	1-10
Y	JP, 9-310066, A (Idemitsu Kosan Co., Ltd.), 02 December, 1997 (02.12.97), especially, Claims; Par. Nos. [0001], [0025] (Family: none)	1-10
Y	JP, 10-316658, A (Mitsubishi Chemical Corporation), 02 December, 1998 (02.12.98), especially, Claims; Par. Nos. [0007] to [0017] (Family: none)	1-10
Y	EP, 517542, A1 (Sumitomo Chemical Company, Limited), 09 December, 1992 (09.12.92), & JP, 5-263073, A & JP, 6-1972, A	1-10
Y	JP, 11-329737, A (Taiho Ind. Co., Ltd.), 30 November, 1999 (30.11.99), especially, Claims; Par. No. [0011] (Family: none)	1-10
Y	EP, 936844, A2 (Junji KIDO), 18 August, 1999 (18.08.99), & JP, 11-233262, A & KR, 99072663, A & CN, 1238655, A	10
X Y	JP, 3-289090, A (Mitsui Toatsu Chem. Inc.), 19 December, 1991 (19.12.91), especially, Claims; page 2, lower left column, line 4 to page 2, lower right column, line 14 (Family: none)	1-6, 9 10